Nonequilibrium mode-coupling theory for uniformly sheared underdamped systems

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Abstract. Mode-coupling theory for uniformly sheared underdamped systems with an isothermal condition is presented. As a result of the isothermal condition, it is shown that the shear stress exhibits significant relaxation at the α-relaxation regime due to the cooling effect which is accompanied by the growth of the current fluctuation. This indicates that nonequilibrium underdamped MCT is not equivalent to the corresponding overdamped MCT, even at long time-scales after the early stage of the β-relaxation. It is verified that the effect of correlations to the density-current modes is, however, negligible in sheared thermostated underdamped systems.

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INTRODUCTION

Glassy liquids are extensively studied for understanding the transition from liquid to amorphous solid states. Two typical theoretical approaches coexist in these studies; the mode-coupling theory (MCT) [1], and the replica theory with assumptions on the metastable states from the random-first-order transition theory (RFOT) [2]. Though not yet complete, the relation between the above two approaches has been revealed in some aspects [2, 3]. For instance, it has been shown that the equation for the non-ergodic parameter (NEP) in MCT can be partly derived by the replica theory [2]. However, since the replica theory is a static theory, it lacks genuinely dynamical effects, and its application to the study of dynamics, e.g. relaxation towards steady state, or response, is difficult.

MCT, which is a dynamical theory, also suffers from difficulties when applied to glassy liquids. For instance, it predicts unphysical non-ergodic transition, which cannot be observed in realistic thermal systems [4, 5]. Another issue is the lack of a consistent perturbative field-theoretic formulation, which is practically applicable to higher orders. Although efforts have been made [6, 7, 8, 9], they are still not comparable to the conventional approach of projection operators and the Mori-type equations [10], which we adopt in this work.

Glassy liquids can be classified into two categories; one is molecular glasses, which is described by Newtonian dynamics, and the other is colloidal glasses, which is described by Brownian dynamics, at the microscopic level, respectively. Historically, MCT for molecular glasses has been developed, and has passed various tests concerning the two-step relaxation phenomena [1]. Then, it was shown theoretically that the MCT for colloidal glasses are equivalent to that for the molecular glasses in the long-time limit [11]. That is, the height of the plateau of the density time-correlator at the β-relaxation regime (NEP), and the α-relaxation time, are coincident. This fact has been verified by molecular dynamics (MD) simulations [12]. Since then, it has been believed that the glassy behavior is insensitive to its microscopic origin.

However, the established equivalency between the two categories is only verified for *equilibrium* MCT, and is not yet established for *nonequilibrium* MCT. It is nontrivial whether nonequilibrium MCT for underdamped systems, such as sheared molecular liquids or granular matters, share equivalent long-time behaviors with that for overdamped systems.

Nonequilibrium MCT for uniformly sheared *overdamped* systems, for e.g. colloidal suspensions immersed in solvents, has been worked out by the pioneering papers of Fuchs and Cates [13, 14] and Miyazaki *et al.* [15, 16]. In these works, it has been shown that the shear thinning and the emergence of the yield stress in glassy states can be captured within this framework. Furthermore, comparison of MCT with MD has been performed in Ref. [16], and it has been shown that, aside from the difference in the early stage before the β-relaxation due to inertia effects, the plateau of the density time-correlator coincide with each other.

On the other hand, nonequilibrium MCT for uniformly sheared *underdamped* systems has been formulated by Chong and Kim [17], whose microscopic dynamics is described by the SLLOD equations [18]. However, there were some problems in this formulation, as indicated in Ref. [19], and calculations to verify its validity have not yet been performed. In contrast to equilibrium MCT and

sheared overdamped MCT, where the temperature is a mere parameter, the temperature is a dynamic variable in sheared underdamped MCT. Hence, it is necessary to control the temperature to avoid heat-up or cool-down in order to conform with realistic physical situations. One of the problems of Ref. [17] is that the temperature is not controlled and heats up.

In this paper, we formulate the MCT for uniformly sheared *underdamped* systems with an isothermal condition imposed. We present that there is a significant relaxation in the shear stress at the α-relaxation regime, although the profile of the density time-correlator is coincident with the overdamped systems after the early stage of the β-relaxation. Then, we address another issue specific to underdamped systems: the significance of correlations to the density-current modes. We show that they are negligible in sheared underdamped thermostated systems, but discuss that this situation might be accidental. This result is new, which has not been discussed in Ref. [19].

We stress that this paper is related to our previous paper [19] in some respects, but it addresses issues not included there, such as the effect of the density-current correlation, as well. We also point out that our formulation of the underdamped MCT developed in this paper can resolve the problem of the stress overshoot in the α-relaxation regime [20, 21]. It is shown that the overdamped MCT underestimates the stress overshoot compared to MD [20], while it is implied that it is consistent with the Brownian dynamics simulations [21]. Thus, it might well be concluded that the pronounced stress overshoot in molecular liquids than in colloidal suspensions is the result of the inertia effect.

UNDERDAMPED ISOTHERMAL MCT

In this section, we present the MCT of uniformly sheared underdamped systems, with isothermal condition imposed. The basis of the formulation is the microscopic SLLOD equations [18] for a spherical N-body system of mass m,

$$\dot{\boldsymbol{r}}_i(t) = \frac{\boldsymbol{p}_i(t)}{m} + \boldsymbol{\kappa}\cdot\boldsymbol{r}_i(t), \tag{1}$$

$$\dot{\boldsymbol{p}}_i(t) = \boldsymbol{F}_i(t) - \boldsymbol{\kappa}\cdot\boldsymbol{p}_i(t) - \alpha(\boldsymbol{\Gamma})\boldsymbol{p}_i(t), \tag{2}$$

where $i = 1,\cdots,N$, and their corresponding Liouville equations. Here, $\kappa^{\lambda\mu} = \dot{\gamma}\delta^{\lambda x}\delta^{\mu y}$ $(\lambda,\mu = x,y,z)$ is the shear-rate tensor, where $\dot{\gamma}$ is the constant shear rate, and $\boldsymbol{F}_i(t)$ is a conservative force with a soft-core potential whose details are irrelevant in the following discussions. The parameter $\alpha(\boldsymbol{\Gamma})$ in Eq. (2), where $\boldsymbol{\Gamma} \equiv \{\boldsymbol{r}_i,\boldsymbol{p}_i\}_{i=1}^N$ with $\boldsymbol{\Gamma} \equiv \boldsymbol{\Gamma}(0)$, gives the dissipative coupling of the particle with the thermostat. If we impose the isothermal condition, which constrains the kinetic temperature to remain constant from its initial equilibrium value, $\alpha(\boldsymbol{\Gamma})$ should be regarded as a multiplier for this constraint, rather than an independent physical parameter. A representative example of this is the Gaussian isokinetic (GIK) thermostat [22], which is established as one of the most typical thermostat in MD. The specific form of $\alpha(\boldsymbol{\Gamma})$ in this thermostat is

$$\alpha(\boldsymbol{\Gamma}) = \frac{\sum_{i=1}^N \left(\boldsymbol{F}_i\cdot\boldsymbol{p}_i - \dot{\gamma}p_i^x p_i^y\right)}{\sum_{j=1}^N \boldsymbol{p}_j\cdot\boldsymbol{p}_j}, \tag{3}$$

which follows from the constraint $\frac{d}{dt}\sum_{i=1}^N \boldsymbol{p}_i(t)^2 = 0$.

Before the discussion of the isothermal condition in MCT, we address the basics of the sheared underdamped MCT. The major difference of the underdamped to the overdamped MCT is that, besides the density time-correlator $\Phi_{\boldsymbol{q}}(t)$, we should consider the current-density cross time-correlator $H_{\boldsymbol{q}}^{\lambda}(t)$ $(\lambda = x,y,z)$ on the same grounds. A crucial feature of the sheared system is that translational invariance is preserved in the sheared frame, although it is broken in the experimental frame. Hence, Fourier transform in the sheared frame is valid. This leads to the following selection rule of wavevectors for two-point functions, $\left\langle A_{\boldsymbol{k}(t)}(\boldsymbol{\Gamma}(t))B_{\boldsymbol{q}}(\boldsymbol{\Gamma})^*\right\rangle_{\rm eq} = \left\langle A_{\boldsymbol{q}(t)}(\boldsymbol{\Gamma}(t))B_{\boldsymbol{q}}(\boldsymbol{\Gamma})^*\right\rangle_{\rm eq}\delta_{\boldsymbol{k},\boldsymbol{q}}$. Here, $\boldsymbol{q}(t) \equiv \boldsymbol{q} - (\boldsymbol{q}\cdot\boldsymbol{\kappa})t$ is the Affine-deformed wavevector, which incorporates the effect of shearing. This selection rule leads to the following definitions of the above two time-correlators,

$$\Phi_{\boldsymbol{q}}(t) \equiv \frac{1}{N}\left\langle n_{\boldsymbol{q}(t)}(t)n_{\boldsymbol{q}}(0)^*\right\rangle_{\rm eq}, \tag{4}$$

$$H_{\boldsymbol{q}}^{\lambda}(t) \equiv \frac{i}{N}\left\langle j_{\boldsymbol{q}(t)}^{\lambda}(t)n_{\boldsymbol{q}}(0)^*\right\rangle_{\rm eq}, \tag{5}$$

where $n_{\boldsymbol{q}}(t) \equiv \sum_{i=1}^N e^{i\boldsymbol{q}\cdot\boldsymbol{r}_i(t)} - N\delta_{\boldsymbol{q},0}$ and $j_{\boldsymbol{q}}^{\lambda}(t) \equiv \sum_{i=1}^N p_i^{\lambda}(t)e^{i\boldsymbol{q}\cdot\boldsymbol{r}_i(t)}/m$ are the density and the current-density fluctuations, respectively. These definitions are not equivalent to those of Ref. [17], where Fourier transform is performed in the experimental frame.

Now we discuss the implementation of the isothermal condition. The most straightforward and rigorous way to perform this is to adopt as $\alpha(\boldsymbol{\Gamma})$ the one for the GIK thermostat, Eq. (3). If this is possible, the resulting Liouville and Mori-type equations are expected to automatically satisfy the isothermal condition. To rephrase it, not only the *averaged* temperature, but also the *microscopic* temperature, is expected to remain constant. However, this does not fit MCT, because the integral of a rational function of momentum, Eq. (3), with Gaussian weight is difficult to perform explicitly. Hence, we propose another way, which only requires the *averaged* temperature to remain constant. This is attained by requiring the isothermal condition to be satisfied at the level of the Mori-type

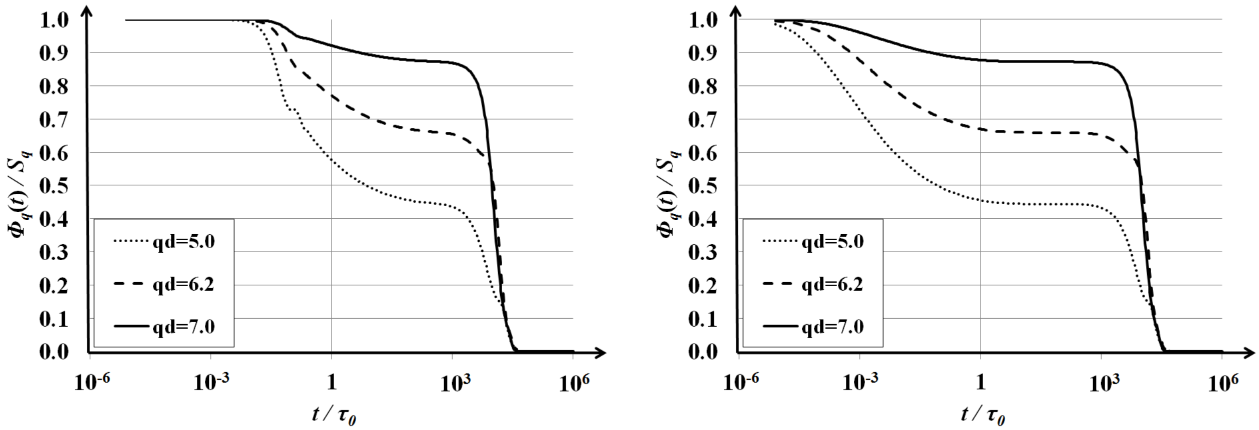

FIGURE 1. Time-evolution of the normalized density time-correlator $\Phi_q(t)/S_q$. The left (right) figure is for the underdamped (overdamped) systems. Time is scaled in unit of $\tau_0 \equiv d/v_0$, where d is the diameter of the spherical particle and v_0 is the relative shear velocity at the boundaries. The three lines correspond to nondimensionalized wavenumbers $qd = 5.0, 6.2, 7.0$. The shear rate $\dot{\gamma}$ is chosen as $\dot{\gamma}\tau_0 = 10^{-4}$, and the volume fraction φ is chosen as $\varepsilon \equiv (\varphi - \varphi_c)/\varphi_c = +10^{-3}$, where $\varphi_c \simeq 0.516$ is the critical volume fraction of the equilibrium MCT transition.

equation, which is an equation for the averaged time-correlator.

The averaged temperature is defined by $\langle T(t)\rangle_{\rm eq} \equiv 2\langle K(\mathbf{\Gamma}(t))\rangle_{\rm eq}/(3Nk_B)$, where $K(\mathbf{\Gamma}) \equiv \sum_{i=1}^N \boldsymbol{p}_i^2/(2m)$ is the total kinetic energy, and $\langle\cdots\rangle_{\rm eq}$ represents the equilibrium ensemble average. The time derivative of the averaged temperature can be obtained from the generalized Green-Kubo formula [23], and the isothermal condition reads

$$\frac{d}{dt}\langle T(t)\rangle_{\rm eq} = \frac{2}{3Nk_B}\langle K(\mathbf{\Gamma}(t))\Omega(\mathbf{\Gamma}(0))\rangle_{\rm eq} = 0, \tag{6}$$

where

$$\Omega(\mathbf{\Gamma}) \equiv -\beta V\dot{\gamma}\sigma_{xy}(\mathbf{\Gamma}) - 2\beta\alpha(\mathbf{\Gamma})\delta K(\mathbf{\Gamma}) \tag{7}$$

is the work function. Here, V is the volume of the system, $\beta \equiv 1/(k_B T_{\rm eq})$ is the inverse equilibrium temperature, $\delta K(\mathbf{\Gamma})$ is the fluctuation of the kinetic energy, and $\alpha(\mathbf{\Gamma})$ is a multiplier for the constraint Eq. (6) which appears in the Liouvillian, whose explicit form is discussed below. The work function $\Omega(\mathbf{\Gamma})$ represents the gross work loaded on the system by shearing and the dissipative coupling to the thermostat.

By introducing general time-correlators of the form

$$G_{A,B}(t) \equiv \langle A(\mathbf{\Gamma}(t))B(\mathbf{\Gamma})\rangle_{\rm eq} = \langle [U(t)A(\mathbf{\Gamma})]\,B(\mathbf{\Gamma})\rangle_{\rm eq}, \tag{8}$$

where $U(t)$ is the time-evolution operator, the isothermal condition Eq. (6) is written in terms of these time-correlators as

$$\dot{\gamma}G_{K,\sigma}(t) + 2G_{K,\alpha\delta K}(t) = 0. \tag{9}$$

This condition indicates a balance between the average work by shearing and the average dissipation. We introduce a multiplier for the constraint Eq. (9) in $G_{K,\alpha\delta K}(t)$, which we denote by $\lambda_\alpha(t)$. This is attained by defining a "renormalized" time-evolution operator $U_R(t) \equiv \lambda_\alpha(t)U(t)$, and a corresponding time-correlator $G^{(\lambda)}_{K,\alpha\delta K}(t)$, where

$$\begin{aligned} G^{(\lambda)}_{K,\alpha\delta K}(t) &\equiv \langle [U_R(t)K(\mathbf{\Gamma})]\,\alpha(\mathbf{\Gamma})\delta K(\mathbf{\Gamma})\rangle_{\rm eq} \\ &= \lambda_\alpha(t)G_{K,\alpha\delta K}(t), \end{aligned} \tag{10}$$

with which we recast Eq. (9) as

$$\dot{\gamma}G_{K,\sigma}(t) + 2G^{(\lambda)}_{K,\alpha\delta K}(t) = 0. \tag{11}$$

Note that $\lambda_\alpha(t)$ is a multiplier which is averaged and appears in the Mori-type equations, and hence independent of $\mathbf{\Gamma}$. From Eqs. (10) and (11), we can see that the isothermal condition is satisfied by choosing $\lambda_\alpha(t)$ as

$$\lambda_\alpha(t) = -\frac{\dot{\gamma}}{2}\frac{G_{K,\sigma}(t)}{G_{K,\alpha\delta K}(t)}, \tag{12}$$

if $G_{K,\alpha\delta K}(t) \neq 0$. On the other hand, if $G_{K,\alpha\delta K}(t) = 0$, the system lacks cooling, and it inevitably heats up.

The Mori-type equations for the correlators $\Phi_{\boldsymbol{q}}(t)$ and $H^\lambda_{\boldsymbol{q}}(t)$ are derived by introducing the projection operator,

$$\mathscr{P}(t)X = \sum_{\boldsymbol{k}} \frac{\left\langle X n^*_{\boldsymbol{k}(t)}\right\rangle_{\rm eq}}{NS_{k(t)}} n_{\boldsymbol{k}(t)} + \sum_{\boldsymbol{k}} \frac{\left\langle X j^{\lambda *}_{\boldsymbol{k}(t)}\right\rangle_{\rm eq}}{Nv_T^2} j^\lambda_{\boldsymbol{k}(t)}. \tag{13}$$

Here, S_k is the static structure factor and $v_T \equiv \sqrt{T_{\rm eq}/m}$ is the thermal velocity, where $T_{\rm eq}$ is the initial equilibrium

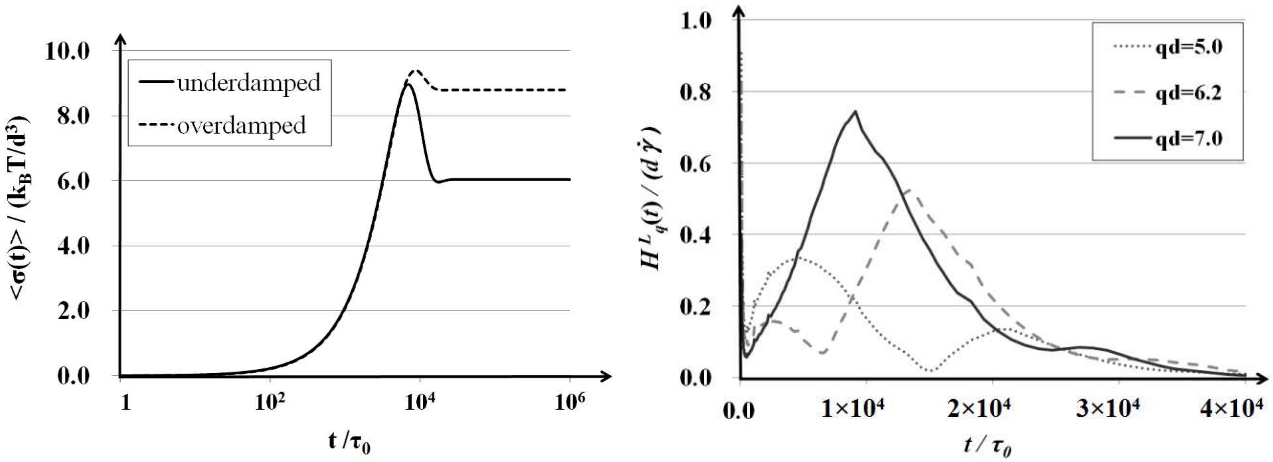

FIGURE 2. Time-evolution of the average shear stress (left) and the longitudinal component of the current-density cross time-correlator $H^L_q(t)$ (right). In the underdamped case, the shear stress is significantly relaxed at the α-relaxation regime, which is accompanied by a growth of $H^L_q(t)$. The shear rate is chosen as $\dot{\gamma}\tau_0 = 10^{-4}$, and the volume fraction as $\varepsilon = (\varphi - \varphi_c)/\varphi_c = +10^{-3}$.

kinetic temperature. To proceed further, it is necessary to resort to the mode-coupling approximation, which determines the specific choice of $\alpha(\mathbf{\Gamma})$ and $\lambda_\alpha(t)$, and provides a closure of the Mori-type equations. To this end, the second projecton operator to the pair-density modes

$$\mathscr{P}_{nn}(t)X = \sum_{\boldsymbol{k}>\boldsymbol{p}} \frac{\left\langle X n^*_{\boldsymbol{k}(t)} n^*_{\boldsymbol{p}(t)} \right\rangle_{\mathrm{eq}}}{N^2 S_{k(t)} S_{p(t)}} n_{\boldsymbol{k}(t)} n_{\boldsymbol{p}(t)} \tag{14}$$

is introduced. The validity of this choice will be discussed in the next section. The simplest form of $\alpha(\mathbf{\Gamma})$ is $\alpha(\mathbf{\Gamma}) = \alpha_0 = \text{const.}$, where no fluctuation is incorporated. This is the choice adopted in Ref. [17]. However, we have figured out that this choice leads to $G_{K,\alpha\delta K}(t) = 0$; the isothermal condition cannot be satisfied, and the system heats up. Hence, it is necessary to incorporate fluctuations into $\alpha(\mathbf{\Gamma})$. In this respect, the simplest form would be

$$\alpha(\mathbf{\Gamma}) = \frac{\alpha_0}{\frac{3}{2} N k_B T_{\mathrm{eq}}} \sum_i \frac{\boldsymbol{p}_i^2}{2m}, \tag{15}$$

where current fluctuations are incorporated. Here, α_0 is a constant. With this choice, it can be verified that $G_{K,\alpha\delta K}(t) \neq 0$, and hence the constraint Eq. (11) can be satisfied. Straightforward calculation of $G_{K,\alpha\delta K}(t)$ and $G_{K,\sigma}(t)$ leads to

$$\lambda_\alpha(t)\alpha_0 = \frac{\dot{\gamma}}{2} \frac{\sum_{\boldsymbol{k}>0} \frac{1}{S_{k(t)} S_k} W_{\boldsymbol{k}} \Phi_k(t)^2}{\sum_{\boldsymbol{k}>0} \frac{1}{S_{k(t)} S_k} \Phi_k(t)^2}, \tag{16}$$

where $W_{\boldsymbol{k}} \equiv \frac{k^x k^y}{k} \frac{1}{S_k} \frac{\partial S_k}{\partial k}$ [19]. This expression corresponds to $\alpha(\mathbf{\Gamma})$ of the GIK thermostat; it is a ratio of the work loaded on the system (numerator) to the total kinetic energy (denominator).

Now we present the Mori-type equation with the mode-coupling approximation applied. We adopt the isotropic approximation, in which case the two Mori-type equations can be cast in a single second-order equation for $\Phi_q(t)$,

$$\begin{aligned} \frac{d^2}{dt^2}\Phi_q(t) \; &= \; -\left[\lambda_\alpha(t)\alpha_0 - \dot{\gamma}\frac{\frac{2}{3}\dot{\gamma}t}{1+\frac{1}{3}(\dot{\gamma}t)^2}\right]\frac{d}{dt}\Phi_q(t) \\ &\quad -v_T^2 \frac{q(t)^2}{S_{q(t)}}\Phi_q(t) - \int_0^t ds M_{q(s)}(t-s)\frac{d}{ds}\,\Phi_q(s), \end{aligned} \tag{17}$$

where the multiplier $\lambda_\alpha(t)$ appears as an effective friction coefficient. It is notable that the memory kernel is unaltered by the introduction of the multiplier with the choice of the second projection operator Eq. (14). In the isotropic approximation, only the longitudinal component of the current-density cross time-correlator, $H^L_q(t) = d\Phi_q(t)/dt$, is considered. The numerical solution of Eq. (17) is shown in Fig. 1, together with the corresponding result for the overdamped case. As can be seen, the long-time behavior after the early stage of the β-relaxation, namely the height of the plateau of the density time-correlator and the α-relaxation time, is equivalent for the two cases.

Despite this fact, there is a significant difference between underdamped and overdamped MCT for sheared systems. From the generalized Green-Kubo formula, the following formula for the shear stress can be derived for the underdamped case [19],

$$\langle\sigma(t)\rangle_{\mathrm{eq}} = \frac{k_B T_{\mathrm{eq}}}{2}\int_0^t ds \int \frac{d^3\boldsymbol{k}}{(2\pi)^3}$$

$$\times \frac{W_{\boldsymbol{k}(s)}}{S_{k(s)}} \frac{\dot{\gamma} W_{\boldsymbol{k}} - 2\lambda_\alpha(s)\alpha_0}{S_k} \Phi_{\boldsymbol{k}}(s)^2. \quad (18)$$

The corresponding well-known formula for the overdamped case [13] can be obtained by setting $\lambda_\alpha(t)\alpha_0 = 0$ in Eq. (18). This term with $\lambda_\alpha(t)\alpha_0$ is exactly the "cooling effect" specific for sheared underdamped systems, which prevents the system from heating up. The numerical result of Eq. (18), together with that of $H^L_q(t)$, is exhibited in Fig. 2. We can see that, in the underdamped case, there is a significant relaxation of the shear stress in the α-relaxation regime. Furthermore, this relaxation is accompanied by a growth of $H^L_q(t)$. From these results, we can obtain an intuitive picture as follows; during the β-relaxation regime, the particles are caged by their neighbors, and they are almost frozen. When the accumulated strain by shearing becomes comparable to the particle size, the cage is broken, and the partiles start to escape from the cage. This generates current fluctuations, which is cooled to keep the temperature of the system unchanged. This cooling effect leads to a relaxation of the system to the genuine stable state, and a stress relaxation occurs.

It is remarkable that the overdamped MCT underestimates the stress overshoot in the α-relaxation regime compared to its corresponding MD [20]. On the other hand, it is impled that the overdamped MCT predicts the magnitude of the stress overshoot consistently with the Brownian dynamics simulations [21]. This consistency is established by means of the schematic model, rather than the microscopic model, of the MCT, so a complete verification remains to be a future problem. However, we might say that the results of Refs. [20] and [21] strongly suggest that the pronounced stress overshoot in molecular liquids than in colloidal suspensions is the result of the inertia effect.

EFFECT OF DENSITY-CURRENT MODES

In the previous section, we have addressed a problem specific to the sheared underamped MCT; that is, to control the temperature from heating-up or cooling-down. There is another non-trivial problem specific to the sheared underdamped MCT which should be addressed; "up to what degree should we take correlations into account?". The fundamental concept of MCT is to take into account correlations with "slow" modes. In the overdamped case, it is the density fluctuation $n_{\boldsymbol{q}}(t)$, and in the underdamped case, it is $n_{\boldsymbol{q}}(t)$ and the current-density fluctuation $j^\lambda_{\boldsymbol{q}}(t)$. Although $j^\lambda_{\boldsymbol{q}}(t)$ is "faster" than $n_{\boldsymbol{q}}(t)$, it is necessary to incorporate to deal with physical phenomena such as stress relaxation at the α-relaxation regime, which we have shown in the previous section. Incorporating correlations, or projecting onto $n_{\boldsymbol{q}}(t)$ and/or $j^\lambda_{\boldsymbol{q}}(t)$, leads to the Mori-type equations, which includes a memory kernel as a time-correlator of noises (uncorrelated degrees of freedom). A memory kernel includes higher-order correlations, and we should extract these correlations by projecting onto higher-order modes, such as nn, nj, nnn, $\cdots$. (Of course, correlations with higher-order modes correspond to multi-body correlations, which must be truncated to close the equation. MCT is a scheme which approximates a four-body correlation by factorizing it into a product of two-body correlations.) For this purpose, we have introduced the second projection operator Eq. (14), which is conventional in equilibrium as well as in sheared overdamped MCT. However, in the sheared underdamped MCT, it is not *a priori* apparent that the projection onto the density-current modes

$$\mathscr{P}_{nj}(t)X \;\equiv\; \sum_{\boldsymbol{k},\boldsymbol{p}} \frac{\left\langle X n^*_{\boldsymbol{k}(t)} j^{\lambda *}_{\boldsymbol{p}(t)} \right\rangle}{N^2 S_{k(t)} v_T^2} n_{\boldsymbol{k}(t)} j^\lambda_{\boldsymbol{p}(t)} \quad (19)$$

is negligible compared to $\mathscr{P}_{nn}(t)$, and hence the adoption of Eq. (14) must be validated. In particular, we should carefully check the roles of $\mathscr{P}_{nj}(t)$ as well as the self-consistency of our argument in the previous section in our underamped MCT, because the existence of the momentum current causes some essential differences in the long-time dynamics from that in the overdamped MCT. In this section, we discuss the effect of the projection onto the density-current modes in the second projection operator, Eq. (20).

Let us consider a second projection operator $\mathscr{P}_2(t)$ of the following form [24],

$$\mathscr{P}_2(t) \;=\; \mathscr{P}_{nn}(t) + \mathscr{P}_{nj}(t), \quad (20)$$

where $\mathscr{P}_{nn}(t)$ and $\mathscr{P}_{nj}(t)$ are defined by Eqs.(14) and (20), respectively. We note that the isothermal condition Eq. (11) and the stress formula Eq. (18) are unaltered by the introduction of $\mathscr{P}_{nj}(t)$. Crucial observation for this property is that the following equalities hold, $\mathscr{P}_{nj}(t)\sigma_{xy}(\boldsymbol{\Gamma}) = 0$, $\mathscr{P}_{nj}(t)K(\boldsymbol{\Gamma}) = 0$, and $\mathscr{P}_{nj}(t)\left[\alpha(\boldsymbol{\Gamma})\delta K(\boldsymbol{\Gamma})\right] = 0$, which follow from the vanishing of ensemble averages with odd number of momentum variables. Here, the explicit form Eq. (15) of $\alpha(\boldsymbol{\Gamma})$ is assumed. As a result, the time-correlators $G_{K,\sigma}(t)$, $G_{K,\alpha\delta K}(t)$, $G_{\sigma,\sigma}(t)$, and $G_{\sigma,\alpha\delta K}(t)$ remain unchanged. The isothermal condition and the stress formula are expressed in terms of $G_{K,\alpha\delta K}(t)$, $G_{\sigma,\alpha\delta K}(t)$ and $G_{K,\sigma}(t)$, $G_{\sigma,\sigma}(t)$, respectively, so the above statement is proved.

Corrections due to $\mathscr{P}_{nj}(t)$ arise in the Mori-type equations for the time-correlators. The introduction of $\mathscr{P}_{nj}(t)$ requires us to introduce two additional time-correlators defined as follows,

$$\bar{H}^\lambda_{\boldsymbol{q}}(t) \;\equiv\; \frac{i}{N} \left\langle n_{\boldsymbol{q}(t)}(t) j^{\lambda *}_{\boldsymbol{q}}(0) \right\rangle, \quad (21)$$

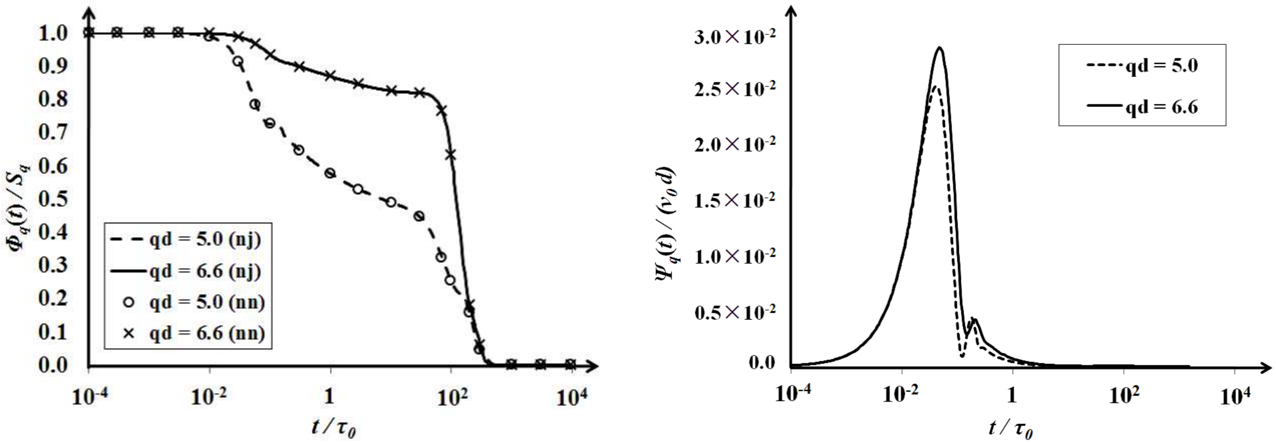

FIGURE 3. Numerical results for the time-correlators $\Phi_q(t)$ (left) and $\Psi_q(t)$ (right). In the left figure, solid and dashed lines with caption (nj) are the solutions of Eq. (25) with $\mathscr{P}_2(t) = \mathscr{P}_{nn}(t) + \mathscr{P}_{nj}(t)$, while circles and crosses with caption (nn) are the solutions for $\mathscr{P}_2(t) = \mathscr{P}_{nn}(t)$.

$$C^{\lambda\mu}_{\boldsymbol{q}}(t) \equiv \frac{1}{N}\left\langle j^{\lambda}_{\boldsymbol{q}(t)}(t) j^{\mu *}_{\boldsymbol{q}}(0)\right\rangle, \qquad (22)$$

in addition to the previously introduced $\Phi_{\boldsymbol{q}}(t)$ and $H^{\lambda}_{\boldsymbol{q}}(t)$, which are defined in Eqs. (4) and (5), respectively. Note that $H^{\lambda}_{\boldsymbol{q}}(t)$ and $\bar{H}^{\lambda}_{\boldsymbol{q}}(t)$ are inequivalent, since sheared systems do not possess translational and reversal symmetries in time. Similarly to $\Phi_{\boldsymbol{q}}(t)$ and $H^{\lambda}_{\boldsymbol{q}}(t)$, we adopt the isotropic approximation for $\bar{H}^{\lambda}_{\boldsymbol{q}}(t)$ and $C^{\lambda\mu}_{\boldsymbol{q}}(t)$. By introducing two scalar time-correlators, $\Psi_q(t)$ and $C_q(t)$, it reads

$$\bar{H}^{\lambda}_{\boldsymbol{q}}(t) \simeq -q(t)^{\lambda}\Psi_q(t), \qquad (23)$$

$$C^{\lambda\mu}_{\boldsymbol{q}}(t) \simeq \delta^{\lambda\mu}C_q(t). \qquad (24)$$

By this approximation, it is possible to derive the following equations for the time-correlators,

$$\begin{aligned}\frac{d^2}{dt^2}\Phi_q(t) &= -v_T^2\frac{q(t)^2}{S_{q(t)}}\Phi_q(t)\\ &\quad -\left[\lambda_\alpha(t)\alpha_0 - 2f_1(\dot\gamma,t)\right]\frac{d}{dt}\Phi_q(t)\\ &\quad -\int_0^t ds M_{\boldsymbol{q}(s)}(t-s)\frac{d}{ds}\Phi_q(s), \qquad (25)\end{aligned}$$

$$\begin{aligned}\frac{d^2}{dt^2}\Psi_q(t) &= -\left[\frac{v_T^2}{3}\frac{q(t)^2}{S_{q(t)}} + \lambda_\alpha(t)\alpha_0 f_1(\dot\gamma,t)\right.\\ &\quad \left. + f_2(\dot\gamma,t)\right]\Psi_q(t)\\ &\quad -\left[\lambda_\alpha(t)\alpha_0 + f_1(\dot\gamma,t)\right]\frac{d}{dt}\Psi_q(t)\\ &\quad -\frac{1}{3}\int_0^t ds M^{\lambda\lambda}_{\boldsymbol{q}(s)}(t-s)\\ &\quad \times\left[\frac{d}{ds}\Psi_q(s) + f_1(\dot\gamma,s)\Psi_q(s)\right], \qquad (26)\end{aligned}$$

where functions $f_1(\dot\gamma,t)$ and $f_2(\dot\gamma,t)$ which incorporate anisotropic effects of shearing are defined as

$$f_1(\dot\gamma,t) \equiv \frac{\frac{1}{3}\dot\gamma^2 t}{1+\frac{1}{3}\dot\gamma^2t^2}, \qquad (27)$$

$$f_2(\dot\gamma,t) \equiv \frac{\frac{1}{3}\dot\gamma^2\left(1-\frac{1}{3}\dot\gamma^2t^2\right)}{\left(1+\frac{1}{3}\dot\gamma^2t^2\right)^2}. \qquad (28)$$

Here, we have eliminated $C_q(t)$ by the relation

$$C_q(t) = \frac{d}{dt}\Psi_q(t) + \frac{1}{2}\frac{\Psi_q(t)}{q(t)^2}\frac{d}{dt}q(t)^2, \qquad (29)$$

which follows from the Mori-type equation. The memory kernel in Eq. (25) consists of two terms, which are given by

$$M_{\boldsymbol{q}}(\tau) \equiv \sum_{i=1,2} M^{(i)}_{\boldsymbol{q}}(\tau),$$

$$\begin{aligned}M^{(1)}_{\boldsymbol{q}}(\tau) &= \frac{nv_T^2}{2q^2}\left[1+\frac{1}{3}(\dot\gamma\tau)^2\right]\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}\\ &\quad\times\left[(\boldsymbol{q}\cdot\boldsymbol{k})c_{\bar{k}(\tau)} + (\boldsymbol{q}\cdot\boldsymbol{p})c_{\bar{p}(\tau)}\right]\left[(\boldsymbol{q}\cdot\boldsymbol{k})c_k + (\boldsymbol{q}\cdot\boldsymbol{p})c_p\right]\\ &\quad\times\Phi_k(\tau)\Phi_p(\tau), \qquad (30)\end{aligned}$$

$$\begin{aligned}M^{(2)}_{\boldsymbol{q}}(\tau) &= -\frac{2\lambda_\alpha(\tau)\alpha_0}{q^2}\left[1+\frac{1}{3}(\dot\gamma\tau)^2\right]\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}\\ &\quad\times\left[(\boldsymbol{q}\cdot\boldsymbol{k})c_{\bar{k}(\tau)} + (\boldsymbol{q}\cdot\boldsymbol{p})c_{\bar{p}(\tau)}\right](\boldsymbol{q}\cdot\boldsymbol{p})\\ &\quad\times\Phi_k(\tau)\Psi_p(\tau). \qquad (31)\end{aligned}$$

Note that the first term $M^{(1)}_{\boldsymbol{q}}(\tau)$ is nothing but the conventional memoery kernel familiar in equilibrium as well as in sheared overdamped MCT, which is the source of the

plateau in the density time-correlator. The second term $M_{\boldsymbol{q}}^{(2)}(\tau)$ is the novel therm which originates in the "cooling effect" due to the isothermal condition. The memory kernel in Eq. (26), which is the trace of $M_{\boldsymbol{q}}^{\lambda\mu}(\tau)$, also consists of two terms, which are given by

$$
\begin{aligned}
M_{\boldsymbol{q}}^{\lambda\lambda}(\tau) &= \sum_{i=1,2} M_{\boldsymbol{q}}^{(i)\lambda\lambda}(\tau), \\
M_{\boldsymbol{q}}^{(1)\lambda\lambda}(\tau) &= \frac{nv_T^2}{2}\int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\left[\boldsymbol{k}c_k+\boldsymbol{p}c_p\right]\cdot\left[\boldsymbol{k}c_{\bar{k}(\tau)}+\boldsymbol{p}c_{\bar{p}(\tau)}\right] \\
&\quad \times\Phi_k(\tau)\Phi_p(\tau), \qquad (32) \\
M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau) &= -2\lambda_\alpha(\tau)\alpha_0\left[1+\frac{1}{3}(\dot{\gamma}t)^2\right]\int\frac{d^3\boldsymbol{k}}{(2\pi)^3} \\
&\quad \times\boldsymbol{p}\cdot\left[\boldsymbol{k}c_{\bar{k}(\tau)}+\boldsymbol{p}c_{\bar{p}(\tau)}\right]\Phi_k(\tau)\Psi_p(\tau), \qquad (33)
\end{aligned}
$$

where again the second term originates in the "cooling effect". The two correlators $\Phi_q(t)$ and $\Psi_q(t)$ couple through $M_{\boldsymbol{q}}^{(2)}(\tau)$ and $M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau)$. The derivation of Eqs. (25)–(33) is somewhat lengthy, though straightforward, so we present only the results.

It should be noted that, in the absense of the coupling to the thermostat, $M_{\boldsymbol{q}}^{(2)}(\tau)$ and $M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau)$ vanish. This suggests that the memory kernel is coincident for the equlibrium underdamped and overdamped MCT, even when projection onto the density-current modes $\mathscr{P}_{nj}(t)$ is included. This proves the validation of the projection onto the pair-density modes $\mathscr{P}_{nn}(t)$ in the equilibrium underdamped MCT.

The numerical solutions of Eqs. (25) and (26) are shown in Fig. 3. For the density time-correlator $\Phi_q(t)$, the results for the case without including $\mathscr{P}_{nj}(t)$, i.e. $\mathscr{P}_2(t)=\mathscr{P}_{nn}(t)$, are plotted in circles and crosses. The initial conditions are chosen as follows:

$$
\begin{aligned}
\Phi_q(t=0) &= S_q, \quad \left[\frac{d}{dt}\Phi_q(t)\right]_{t=0}=0, \qquad (34) \\
\Psi_q(t=0) &= 0, \quad \left[\frac{d}{dt}\Psi_q(t)\right]_{t=0}=\frac{k_BT}{m}. \qquad (35)
\end{aligned}
$$

As can be seen from Fig. 3, although a sign of correlation of currents can be seen in $\Psi_q(t)$ (which appears as a peak around $t/\tau_0\simeq 10^{-1}$), the result of $\Phi_q(t)$ is almost coincident with that for $\mathscr{P}_2(t)=\mathscr{P}_{nn}(t)$. Together with the fact that $\mathscr{P}_2(t)$ of Eq. (20) leads to the identical isothermal condition and the stress formula as for $\mathscr{P}_2(t)=\mathscr{P}_{nn}(t)$, it is verified that projection onto the density-current modes is negligible in sheared thermostated systems as well. Thus, the analysis in the previous section, where we only use $\mathscr{P}_{nn}(t)$ for the second projection operator, is self-consistent.

In principle, we can see from Eqs. (31) and (33) that the "cooling effect" which affects the memory kernel works to destroy the plateau of the density time-correlator, since their contributions are negative. This can be interpreted as the exhausion of the cage by cooling, which allows the caged particles to escape. However, as shown in Fig. 2, $M_{\boldsymbol{q}}^{(2)}(\tau)$ and $M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau)$ becomes significant only at the α-relaxation regime, where the plateau-generating kernels $M_{\boldsymbol{q}}^{(1)}(\tau)$ and $M_{\boldsymbol{q}}^{(1)\lambda\lambda}(\tau)$ decay irrespective of the existence of $M_{\boldsymbol{q}}^{(2)}(\tau)$ and $M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau)$. This is why the effect of $M_{\boldsymbol{q}}^{(2)}(\tau)$ and $M_{\boldsymbol{q}}^{(2)\lambda\lambda}(\tau)$ is hidden behind.

Although the role of $\mathscr{P}_{nj}(t)$ is not significant in the present case, it is an important feature that dissipation acts to destroy the plateau of the density time-correlator. A striking example can be found in granular liquids [25], where the plateau of the density time-correlator is destroyed by inelastic collisions. Hence, we might rather consider that correlations with density-current modes should be included in general, and it might be accidental that they can be neglected in sheared thermostated systems.

Note that the result of $\Psi_q(t)$ (which is essentially $\bar{H}_{\boldsymbol{q}}^{\lambda}(t)$) does not show a growth in the α-relaxation regime, in contrast to $\frac{d}{dt}\Phi_{\boldsymbol{q}}(t)$ (which is essentially $H_{\boldsymbol{q}}^{\lambda}(t)$). This is an explicit manifestation of the inequivalence of $H_{\boldsymbol{q}}^{\lambda}(t)$ and $\bar{H}_{\boldsymbol{q}}^{\lambda}(t)$ mentioned previously.

DISCUSSION AND CONCLUSION

At the formal level, response formulas can be derived from the generaized Green-Kubo (GGK) relation [23, 26]. For the case of constant external fields, this relation gives a formula for the steady-state averages, which characterizes the relaxation towards a steady state. In contrast, for the case of time-dependent external fields, the time-ordering of operators should be handled with care, whose application to the GGK relation is relatively complicated. As an alternative, we have constructed an explicit approximate (quasi-)steady-state distribution function valid on the plaetau of the density time-correlator, and have derived a response formula at the linear order. The situation we consider might be restricted, but at least it is explicitly calculable, and can be compared to experiments.

In conclusion, we have formulated a nonequilibrium MCT for uniformly sheared underdamped systems with an isothermal condition. We have figured out that there is a significant stress relaxation at the α-relaxation regime due to a cooling effect, which is accompanied by the growth of current fluctuations. This stress relaxation is predicted to be larger than that in the overdamped MCT, which is consistent with MD and Brownian dynamics simulations [20, 21]. This indicates that nonequilibrium

underdamped MCT is not equivalent to its corresponding overdamped MCT, even at long time-scales after the early stage of the β-relaxation. This is in sharp contrast to the equilibrium case. We have also shown that correlations with density-current modes are not important in sheared underdamped thermostated systems, but argued that this might be accidental, and they should be incoroprated in general.

Another example which cannot be described by the overdamped formulation is granular particles [25]. The study of rheological properties of granular liquids by means of sheared underdamped MCT presented here is in progress, and will be reported elsewhere [24].

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